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# FORMALDEHYDE MEASUREMENTS BY THE DNPH METHODS: A REVIEW BY THE TESTING AND MONITORING WORKGROUP

## A. Validity of data in the EPA Database

Studies carried out by Radian International for the Gas Research Institute (GRI) have raised questions regarding the validity of aldehyde emission measurements using the CARB 430 procedure[1]. The industry uses CARB 430, EPA 0011, and related 2,4-dinitrophenyl hydrazine (DNPH ) colorimetric procedures to measure formaldehyde emissions from combustion sources. Much of the aldehyde emission data that are available for EPA rule formulation were collected using DNPH procedures. The intent of this memorandum is to provide further guidance to the ICCR Source Groups on deciding which data are valid, and what test methods might be used for future measurements.

The Radian report shows evidence that the problem is related to $NO_2$ (not to be confused with NO or NOx) in the exhaust gas. DNPH reacts with all aldehydes to form derivatives which are then separated and analyzed by liquid chromatography. Radian has also found that DNPH also reacts with $NO_2$ to form a derivative. This side reaction with $NO_2$ can lead to depletion of the DNPH or produce other substances that mask the color that is produced by the aldehyde-DNPH reaction. In general, we recommend that Source Groups should be cautious in their use of CARB 430 data in the EPA data base.

The GRI reported only comparative measurement between the Fourier Transform Infrared (FTIR) analyzer and CARB 430 for natural gas fired internal combustion engines and found discrepancies between data from the two methods only with lean or clean burn engines. The GRI stated that they have "...no evidence of problems with their CARB 430 applications to natural gas-fired boilers, heaters, turbines or rich burn engines." Their data also showed that their CARB 430 data was always in agreement with the FT-IR results when the exhaust gas had less that 60 ppm of $NO_2$. Their data does not suggest that CARB 430 data should rejected on the basis of $NO_2$ interferences as long as the exhaust gas contains no more than 60 ppm $NO_2$ in the flue gas. The ICCR Source Groups may in fact be able to supply evidence that the exhaust gas from their sources do not exceed 60 ppm $NO_2$ thereby dispelling concerns about the validity of the CARB 430 data from their emission sources, or certain groups of their emission sources. The data should, of course, still be subjected to the usual engineering and statistical reviews before it is used in the rule making process.

During our review of the Radian study, it became evident that the Radian used formaldehyde concentrations found by FTIR to determine the sampling volumes used for the CARB 430 measurements in order to ensure that sufficient excess of DNPH would be present to react with formaldehyde. Since at that time they had not yet learned of the $NO_2$ interference, they inadvertently used too large a sampling volume. A closer review of CARB 430 indicates that the method does not specify volume of stack gas to be sampled. It is therefore possible that some of the data present in the EPA data base collected by CARB 430 may indeed be valid, even if the $NO_2$ levels were high. However, in the absence of specific information about $NO_2$ levels and sampling volumes for these tests, we believe that it is likely that these tests underestimate formaldehyde emissions from lean or clean burn engines.

## B. Future Tests with DNPH Methods

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[1] A September 11, 1996 letter to Ms. Amanda Agnew of the EPA from Mr. James M. McCarthy of the GRI regarding Internal Combustion Engine Test Methods.

The results of these field test show that formaldehyde emissions are likely to understated when determined by routine application of CARB 430 to lean or clean burn engines emitting high levels of NOx, in particular $NO_2$ . Operators of these type of sources should check their $NO_2$ emissions prior to doing any formaldehyde measurements to see if they have a potential problem. This can be accomplished using a portable NOx analyzer that provides NO and $NO_2$ data. The test contractor may than be able to adjust the sampling volume accordingly in order to avoid depletion of the DNPH by $NO_2$ .

Recent laboratory tested reported to GRI have succeeded in reproducing the step change decrease in formaldehyde concentrations when $NO_2$ concentration exceed 60 ppm. This was achieved by having the gas matrix containing formaldehyde and $NO_2$ more closely resemble that present in actual combustion gas emissions (i.e., including $CH_4$, CO, $CO_2$, NO, etc). This will permit the GRI to undertake laboratory experiments in the next few weeks that evaluate the Ashland and Celanese methods. Field studies evaluating these methods are planned in August-September 1997. The goal of these studies is to arrive at a cost effective method that will result in accurate measurements of formaldehyde emissions without necessarily having to employ the more expensive FTIR technique.

Our recommendation is that the DNPH procedures should not be rejected for future testing applications because of interferences that were observed with the lean and clean burn two-cycle internal combustion engines. Future testing is expected to result in an improved DNPH method which avoids interference present in emissions with high $NO_2$ levels. In addition, industry is also evaluating alternative procedures such as the Ashland method, a DNPH impregnated sorbent cartridge, and the Celanese method, an aqueous impingers techniques that measure total aldehydes.